

spectrum at room temperature (Swalen, 1960), for such a spectrum would not be observed if the octahedron were perfect. The Co-Cl distance of 2.47 Å is somewhat longer than would be expected on the basis of the sum (2.3 Å) of the cobalt octahedral radius and the chlorine radius (Pauling, 1960), but agrees well with the value of 2.49 Å found by Dunitz (1957) in α -cobalt dipyridine dichloride. The bonding along the $\text{Co}(\text{AlCl}_4)_2$ chains is very compact; the inter-chain bonding is loose, the shortest Cl-Cl interchain contacts being 3.73 Å.

$\text{Co}(\text{AlCl}_4)_2$ is another of the few exceptions to the rule that octahedral complexes of divalent cobalt are red or pink and tetrahedral complexes blue. However, the symmetry of the structure is sufficiently low so that the degeneracies of the excited energy levels of Co^{+2} are removed, and large shifts in the characteristic absorption bands can occur.

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Refinement of the Structure of BaTiO_3 and other Ferroelectrics

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The structure of BaTiO_3 as determined by Evans (1961) is reliable, provided it is recognized that the thermal parameters, which are all rather small, are not very accurately known. The large standard deviations obtained by use of a least-squares program (Evans, 1961; Geller, 1961) are inconsistent with the terms in which the model is defined; this internal contradiction means that the application of the program to this type of structure is suspect, and cannot be used to discredit the empirical agreement between three independent determinations. The evidence suggests that position parameters may be found with fair confidence, by suitable methods of refinement, even when thermal parameters are doubtful.

Refinement of the structure of BaTiO_3 and other ferroelectrics

It would be a great pity if all the outstandingly careful work of Evans (1961) on the structure of BaTiO_3 led only to the conclusion that 'the structure is essentially indeterminate'. The evidence quoted by Evans himself is against such a conclusion, though it is true that a satisfactory statistical method of estimating the errors in the parameters has not yet been found.

The parameters have been determined in three independent investigations, by Evans (1961), Frazer, Danner & Pepinsky (1955) and Känzig (1951). Evans refined the structure in terms of four different non-cubic models. The results of all six models are recorded in Evans's Table 2. The mean values and mean deviations of the parameters are shown here in Table 1;

the extreme range of the thermal parameters is also shown. It can be seen that there is very reasonable agreement in the position parameters (that for O_2 being least accurate) and that there is order-of-magnitude agreement in the thermal parameters, none of which are abnormally large. It is well known that thermal parameters are particularly sensitive to any disregarded or inadequately corrected systematic errors, such as effects of extinction, absorption, or incorrect scaling; hence it is not really surprising (though it may be disappointing) that agreement between them is not closer. The empirical agreement between position parameters obtained in quite independent investigations, and by refinement of different models, shows that these are not very sensitive to variations in the thermal parameters—a fact also noted by Danner, Frazer & Pepinsky (1960), and

shown by Geller (1961) to be true even in an extreme case in which the thermal parameters proved indeterminate. In the absence of any examples to the contrary, the statement of Evans that 'widely divergent sets [of parameters] will give equally satisfactory agreement' (which in any case depends on the meaning attached to 'widely') cannot be given much weight.

Empirically, therefore, one can say that the structure is reliably known, even though its error is estimated in terms of ranges of possible values rather than of standard deviations. The ranges could be narrowed by omitting the two models with less than 7 parameters. Even as it stands in Table 1, the accuracy of the description is as good as for most carefully-studied oxides; the importance sometimes given in the literature to the discrepancy in the measured values of $z(\text{O}_2)$ is due to a misunderstanding of what we can hope from a structure determination.

Table 1. *Mean values from models 2-6 recorded by Evans (1961)*

	Position parameters		Thermal parameters (in Å ²)		
	Magnitude	Mean deviation	Magnitude	Mean deviation	Range
Ba	0	—	0.30 ₅	0.04 ₃	0.27-0.48
Ti	0.014 ₂	0.000 ₇	0.29 ₇	0.11 ₃	0.13-0.53
O ₁	-0.025 ₃	0.002 ₃	0.50 ₃	0.31 ₈	0.08-0.90
O ₂	-0.012 ₃	0.008 ₂	0.63 ₇	0.20 ₂	0.07-0.90

Against this acceptance of the structure, Evans quotes the standard deviations calculated from 'the diagonal terms of the inverse of the full least-squares matrix' (program by Busing & Levy, 1959). These (σ_5 in his Table 2) are of the order of magnitude of, and sometimes exceed, the corresponding parameters. Hence he concludes that the structure determination is meaningless. But there is a possible alternative conclusion, namely that there is some fault or flaw in the application of the program to structures which 'deviate only by small atomic displacements from a higher symmetry group'. That this latter is true is shown as follows.

Since the symmetry is polar, inversion through a centre gives a structure indistinguishable from the original. To describe the structure, it is therefore necessary to define not only the origin, by choosing arbitrarily the z -parameter of one atom (preferably the heaviest, Ba), but also the sense of the z -axis, by choosing arbitrarily the sign of the z -parameter of another atom (preferably* the next heaviest, Ti).

* Theoretically, any second atom can be chosen to fix the sense of the z -axis. Practically, the choice of an unimportant atom (i.e. an atom with small scattering factor or small displacement) may prevent progress, being comparable to an

From Evans's Table 2, z_{Ti} is +0.012, and its standard deviation is 0.018. This means that there is a moderate probability (about 30%) of the correctness of a structure whose z parameter is -0.006 or less. But this conflicts with the original definition of the sense of the z axis. Whether the program in fact attempts to impose this requirement is not made clear. If it does not, the occurrence of oscillation between the two senses is not surprising. If it does, there is some internal contradiction in the result which makes all other conclusions suspect.

The standard deviations of some of the thermal parameters are also hard to explain. For Ti, B_{33} is 0.30 ± 0.63 ; for O₁, B_{22} is 0.50 ± 0.87 ; for O₂, B_{22} is 0.90 ± 1.48 , B_{33} is 0.90 ± 1.02 . In all these cases there is a moderate or large probability of a negative thermal parameter. Such negative values are actually found in Geller's use of the program (his Tables 6 and 8), where it is noted that they are physically impossible. It is hard to see how a program which allows them to occur can be relied on, since it suggests that the path of refinement deviates so far from the initial model that false minima can easily be reached.

It would be wrong if further work on this important type of structure were discouraged by the failure of one particular refinement procedure. It is all the more necessary to continue to explore other types of approach which may not be subject to the same weaknesses. In particular, the insensitivity of position parameters to alterations of thermal parameters suggests that the former may be found with fair confidence even when the latter are doubtful. Meanwhile there is no reason to doubt the reliability of the BaTiO₃ structure within the parameter range indicated in Evans's Table 2 and summarized in Table 1 of this paper.

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attempt to use second-order corrections in circumstances where the first-order terms have not yet been allowed for. The Ti atom is the obvious one to choose, because of its high atomic number; only if this choice did not lead to a solution would the alternative of holding $z(\text{O}_1)$ negative be worth trying. The making of *some* choice is a necessary condition for progress; whether any particular choice is a sufficient condition can only be tested empirically.